

CHEMICAL COMPOSITION OF TOURMALINES BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS.

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ABSTRACT

In this paper, results of the determination of sixteen elements in the twelve Brazilian tourmaline are reports. These samples were analyzed using by a methodology to determine trace elements in tourmaline by instrumental neutron activation analysis. The interference effect of ¹⁰B was demonstrated by irradiating samples of different weight from the same tourmaline and plotting a graph of specific activity against the sample weight. The ideal weight interval was obtained in the straight line deviation. The interference effect is minimized or eliminated in this weight interval. The ideal weight interval represent “no interference weight” condition. Twelve Brazilian tourmalines from magmatic environment were further analyzed by instrumental neutron activation analysis using no interference weight condition. Radionuclides ⁶⁵Zn, ⁵⁹Fe, ⁶⁰Co, ⁵¹Cr, ⁴⁶Sc, ⁸²Br, ¹⁴⁰La, ^{24m}Na, ⁴²K, ⁸⁵Sr, ¹⁸²Ta, ¹³⁴Cs, ¹²⁴Sb, ¹⁵²Eu, ¹⁴¹Ce and ¹²⁴Sb were detected. ¹⁴⁰La, ¹⁵²Eu, ¹⁴¹Ce, and ⁸²Br showed inadequate sensitivity. Then, it was necessary to tolerate the interference of degree ¹⁰B for these radionuclides analysis.

1. INTRODUCTION

Tourmalines are structurally and chemically complex borosilicate minerals, that occur in many types of rock and environments. Tourmalines are important as petrogenetic indicators because they can incorporate by total or partial substitution of a great variety of chemical elements [1-8]. This paper reports results of the determination of sixteen elements in the twelve Brazilian tourmaline from magmatic environment [9]. This tourmalines samples were analyzed by instrumental neutron activation analysis using the methodology described [10]. INAA in samples containing boron is problematic due to the large neutron-capture cross section of ¹⁰B (3838 barns in thermal energy 0.0253 eV for the ((n,α) reaction). This results in different nuclear production rates in different parts of the samples and this is undesirable. As a consequence of the neutron-capture effect, the concentration of the elements determined by neutron activation is lower than it really. One of them is to use a graph of the specific activity against the sample weight and determine the smallest sample where interference effect is eliminated or minimum. The determination of trace element in tourmalines by neutron activation analysis has been investigated by some authors [11-13]. King et al. studied the REE distribution in tourmalines by INAA technique involving pretreatment by boron volatilization [12]. Jolliff et al. [13] and Laul and Lepel [11] studied the REE distribution in tourmalines by

radiochemical neutron activation analysis. The analytical methods described by these authors are very laborious and contamination may occur. The chemistry composition of Brazilian tourmaline in some pegmatites has been investigated by INAA, Bilal et al. [14]. But there is no reference if the interference effect was considered in that study.

All the tourmaline samples analyzed belong to the elbaite-schorl series. Multi-colored tourmaline is present in several granitic pegmatites. They belong to the Eastern Gemological Provinces. In this gemological province (Northeast of Minas Gerais State, Brazil) different pegmatitic districts are distinguished, representing distinct episodes of granitogenesis within the Neoproterozoic Araçuaí Thrust-Fold Belt [15]. The tourmalines are from Araçuaí pegmatitic district where the bodies usually have a zoned internal structure and are mineralogically complex. This is evidenced by voluminous and frequent metasomatic units. The schorl crystals were collected from the border zone, followed by Li-schorls from the wall zones, Fe-elbaites from intermediate zones and finally, elbaite, from substitution bodies. For more detailed information the authors refer to Castañeda et al. [10].

2. METHODOLOGY DESCRIPTIONS

The methodology used in this work [10] is based on studies for determination of trace-element by INAA when during irradiation there is a suppression of the incident neutron flux in the target sample [16-17]. This interference effect can be demonstrated by irradiating the same sample of different weights and then, after determining the activity of each sample, plotting a graph of specific activity against sample weight. From the graph it is possible to determine the maximum weight where interference effect was eliminated or minimized and thus limit irradiation to the samples of that determined weight. This occurs in the straight line deviation.

2.1. Sampling and Analytical Techniques

Twelve Brazilian tourmalines from granitic pegmatites were carefully selected from several hundreds of fragments based on quality and color homogeneity. Special effort it was also employed to obtain tourmaline without impurity. Selected tourmaline samples were initially powdered using an agate mortar. For INAA the irradiation was performed in the reactor TRIGA Mark I IPR-R1 at 100 kW, with thermal neutron flux of 6.6×10^{11} n.cm².s⁻¹. The acquisition parameters the gamma spectroscopy and the irradiation used were carefully defined in order to better sensitivity. For more detailed information about irradiation and acquisition parameters the gamma spectroscopy the authors refer to Oliveira et al. [9]. Thirty-three powdered samples of the same tourmaline of weight between 0.003-0.45g were irradiated in order to approximate to the “no interference weight” condition. For radionuclides that showed an inadequate sensitivity it was necessary to tolerate higher degrees of interference. Certified reference material, IAEA/Soil-7 was irradiated simultaneously with the tourmaline to provide reproducibility of results of the analysis and for the quality control. Using the “no interference weight” condition, the twelve samples of tourmalines were analyzed by INAA. Two set of investigations were performed. One, designated by set-1, the samples weighed around 0.09g. The other set, designated by set-2, around 0.05g. These two different set, the samples weights are in the weight interval where the interference effect is eliminated or minimized.

3. RESULTS AND DISCUSSION

3.1. Metodology

The graphs of specific activity against sample weight for ^{59}Fe , ^{65}Zn , radionuclides are shown in Fig. 1.

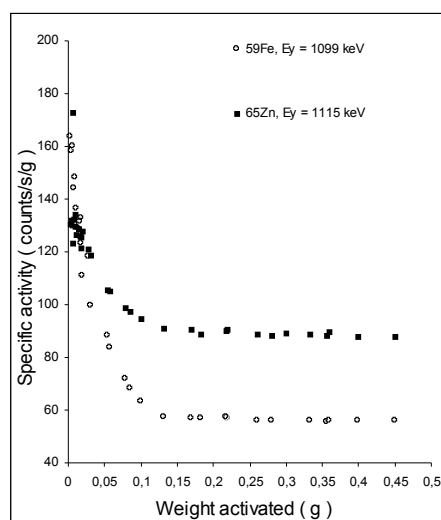


Figure 1. Variation of induced specific activity with weight of tourmaline for ^{59}Fe and ^{65}Zn (CA3qn sample).

The deviation from the straight line, begins at the below 0.1 g weight. So, in tourmaline samples weighing below 0.1g the interference effect is minimized. In order to provide the reproducibility of method and check the interval where the interference effect is minimized, it is important to perform several investigation and plot them as show in Fig. 1. In the tourmaline samples, the radionuclides ^{65}Zn , ^{59}Fe , ^{60}Co , ^{51}Cr , ^{46}Sc , ^{82}Br , ^{140}La , ^{24m}Na , ^{42}K , ^{85}Sr , ^{182}Ta , ^{134}Cs , ^{124}Sb were detected. All radionuclides observed showed good agreement in the deviation from the straight line. Small systematic discrepancy was noted for ^{134}Cs , ^{182}Ta , ^{124}Sb , ^{46}Sc , ^{152}Eu , ^{140}La , due to their low concentration. The isotopes investigated were: ^{187}W , ^{140}La , ^{199}Au , ^{72}Ga , ^{76}As , ^{42}K , ^{131}Ba , ^{75}Se , ^{203}Hg , ^{82}Br , ^{85}Sr , ^{51}Cr , ^{124}Sb , ^{134}Cs , ^{46}Sc , ^{86}Rb , ^{59}Fe , ^{60}Co , ^{182}Ta , ^{233}Pa , ^{65}Zn , ^{110m}Ag , ^{152}Eu , ^{160}Tb , ^{175}Hf , ^{177m}Lu , ^{95}Zr , ^{24m}Na .

3.2. Chemical Analysis

Table 1 shows data by INAA for seven representative tourmaline samples for both two irradiation set: Set-1 for tourmaline weighting around 0.09g and the other, set-2 around 0.05g. Table 1 shows that, generally the concentration for each element in the samples weighing around 0.09g is lower than in the samples weighing around 0.05g. This results suggest that the interference effect still occurs in the samples that weigh around 0.09g. On the other hand, in tourmaline samples weighing around 0.05g the interference effect is minimized. If it occurs it has a lesser extent when compared to the samples weighing around 0.09g. La, Ce, Sm, Eu, Ta, Br and Sb showed an inadequate sensitivity and it was necessary to tolerate the interference degrees. So, the analysis for trace elements should be performed considering the results obtained for tourmaline samples weighing around 0.09g.

Table 1. Analytical results ($\mu\text{g} / \text{g}$) obtained by INAA on representative tourmaline group: elbaite to schorl.

	Schorls				Li-schorl		Fe-elbaite				Elbaite			
	Border and wall zones				Wall zone		Intermediate zone				Replacement bodies and fracture fillings			
	Bu4qN	Bu4qN	PA9	PA9	LA2nes	LA2nes	L2QV	L2QV	PD	PD	MR03	MR03	U1b	U1b
Set	Set-1	Set-2	Set-1	Set-2	Set-1	Set-2	Set-1	Set-2	Set-1	Set-2	Set-1	Set-2	Set-1	Set-2
W (g)	0.0990	0.0488	0.0990	0.0490	0.0980	0.0470	0.0960	0.0470	0.0990	0.0490	0.0980	0.0490	0.0980	0.0480
Sc	0.60 ± 0.07	0.88 ± 0.07	14 ± 1	16 ± 1	2.1 ± 0.1	2.4 ± 0.1								
Cr		nd			23 ± 4	24 ± 8	110 ± 10	83 ± 10	nd	9 ± 2				
Fe (%)	6.4 ± 0.1	6.9 ± 0.1	5.4 ± 0.1	6.0 ± 0.1	4.2 ± 0.1	4.7 ± 0.1	2.2 ± 0.1	2.37 ± 0.01	3.8 ± 0.1	4.1 ± 0.1			0.26 ± 0.01	0.36 ± 0.04
Co	nd	nd	2.0 ± 0.3	2.5 ± 0.4	1.4 ± 0.3	nd	4.0 ± 0.4	4.0 ± 0.4	nd	0.46 ± 0.13				
Zn	1760 ± 30	1930 ± 50	600 ± 20	650 ± 30	1830 ± 30	1990 ± 50	1250 ± 30	1330 ± 10	960 ± 20	1020 ± 20			900 ± 20	1050 ± 40
La	2.76 ± 0.88	nd	1.80 ± 0.26	nd			0.52 ± 0.27	nd			1.24 ± 0.4	nd		
Ce	2.99 ± 0.99	nd	1.99 ± 0.30	nd										
Tb	0.91 ± 0.26	nd	0.95 ± 0.28	0.96 ± 0.29										
Th											0.51 ± 0.1	0.56 ± 0.2	0.61 ± 0.1	0.69 ± 0.2
Ta	16 ± 1	19 ± 1			2.81 ± 0.31	3.14 ± 0.53	1.86 ± 0.32	1.54 ± 0.6	0.93 ± 0.3	1.37 ± 0.21	29 ± 1	48 ± 1	5.2 ± 0.4	5.0 ± 0.6
Na (%)	1.30 ± 0.01	1.50 ± 0.01	1.11 ± 0.01	1.20 ± 0.01	1.46 ± 0.01	1.62 ± 0.01	1.62 ± 0.75	1.75 ± 0.01	1.47 ± 0.01	1.63 ± 0.01	1.01 ± 0.01	1.08 ± 0.01	1.00 ± 0.01	1.17 ± 0.01
Cs	190 ± 10	210 ± 10									12 ± 1	10.1 ± 0.8		
Ga	88 ± 5	85 ± 6	72 ± 5	80 ± 5	150 ± 10	160 ± 10	300 ± 10	320 ± 10	53 ± 3	58 ± 7	120 ± 10	130 ± 10	160 ± 10	150 ± 10
Sb							4.6 ± 0.7	2.7 ± 0.2						
Br		0.22 ± 0.10	nd											

nd = not detected; cc = certified concentration; ci = confidence interval; * = (significance level 0.05); w = weight (g)

All the samples analyzed belong to the elbaite-schorl series, where end-member calculations indicate variations in the Fe_{total} and $Al^{3+}+Li^{+}$ contents (Castañeda et al., 2000; Oliveira et al., 2002). According to the trace elements analysis, the REE contents were not observed any systematic compositional within the zoned internal structure of pegmatites. On the other hand, within the zoned internal structure of pegmatites, the tourmaline samples show small but important differences in their chemical composition. In general, the samples from the wall and border zones show higher concentrations of Sc, Zn and Ga than from the intermediate zones and substitution bodies. The last one seems to be more significant in complex zoned pegmatites, viz., Morro Redondo pegmatite, namely MR samples. The concentrations of Co are just associated to the blue and green crystal hues. On the other hand multicolored tourmalines from the pockets and the quartz-rich core contain higher concentration of Ta. The main differences in the composition of trace elements among the tourmaline samples from different internal zones of pegmatite can be attributed to the direct result of fractional crystallization of batholiths.

4. CONCLUSIONS

When the interference effect of ^{10}B is eliminated or minimized INAA can be used to determine trace element in tourmaline. However, special care should be taken with irradiation, experimental and acquisition parameters, since the sensitivity for trace elements can be affected by the interference effect of ^{10}B . The chemical composition showed that the tourmalines from granitic-pegmatitic have relatively low concentration of minor and trace elements. On the other hand, within the zoned internal structure of pegmatites, the tourmaline samples show important differences in their chemical composition.

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